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(54) Title: METHOD OF IMPROVING ADHESION TO GALVANIZED SURFACES			
(57) Abstract <p>The adhesion between a galvanized surface and a polymeric material is improved by coating the galvanized surface with an adhesion promoter. The adhesion promoter is a compound which includes at least two trialkoxysilyl groups which are bridged together by a compound which includes at least one reactive nitrogen atom. In certain embodiments the galvanized surface is treated with an alkaline cleaner prior to application of the adhesion promoter. The coating composition forms an adhesion promoting coating in either the hydrolyzed or unhydrolyzed form and can further be used on steel, aluminum or brass.</p>			

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METHOD OF IMPROVING ADHESION TO GALVANIZED SURFACES

Galvanized coatings (generally zinc or zinc alloy coatings) are used to prevent rusting of ferrous metals. Galvanized steel is used for a variety of different applications. Galvanized coatings are used on articles which are subjected to moist and sometimes corrosive environments.

In certain applications the galvanized article must be coated with, for example, paints or adhesives. One example of adhesive coated galvanized articles is galvanized collated fasteners such as staples, nails, screws, tacks and the like. When fasteners are used with automatic tools, the individual fasteners are formed and held together using either adhesive or an adhesive tape. When fasteners are stored in a moist environment, moisture can destroy the adhesion between the adhesive and the galvanized surface. This may prevent the fasteners from loading properly or may cause the tool to jam or leave a portion of the adhesive tape on the discharged fastener.

Summary of the Invention

The present invention is premised on the realization that the adhesion between a polymeric coating and a galvanized surface can be improved by coating the galvanized surface with a compound which includes both a nitrogen functionality and a plurality of alkoxy silane functionalities.

More particularly the present invention is premised on the realization that a compound having two or more trialkoxysilyl groups bridged together by a moiety which includes nitrogen, when coated onto a galvanized surface, provides a surface onto which polymeric coatings will remain bonded regardless of humidity. The nitrogen can be a primary or secondary amine, ureido group, an isocyanate or a cyanide group.

This compound can be applied either as an aqueous solution after the galvanized surface has been treated with a base or can be applied as a 100% liquid coating without pretreatment. Thus, the compound can bind to the metal surface without hydrolysis. Further, this compound also improves adhesion to other engineering metals i.e., stainless steel, carbon steel, brass and aluminum. The objects and advantages of the present invention were further appreciated in light of the following detailed description.

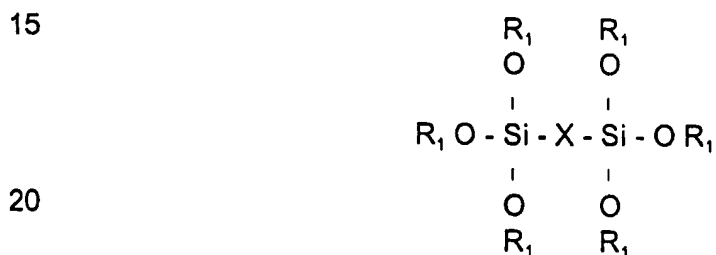
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Detailed Description

The present invention is a method of improving the adhesion between a polymeric coating such as paint, an adhesive or an adhesive tape and a galvanized metal surface.

5 Galvanized references a zinc or zinc alloy coating which is applied to a metal surface generally a ferrous metal surface to prevent the rusting of the metal. Galvanized includes both hot dipped and electro galvanized surfaces. Although the present invention can be utilized to improve the adhesion of any galvanized surface, it is at least in one preferred embodiment used to hold together staples for use in an automatic stapler.

The coating used to improve the adhesion to a galvanized surface according to the present invention has the following general formula.



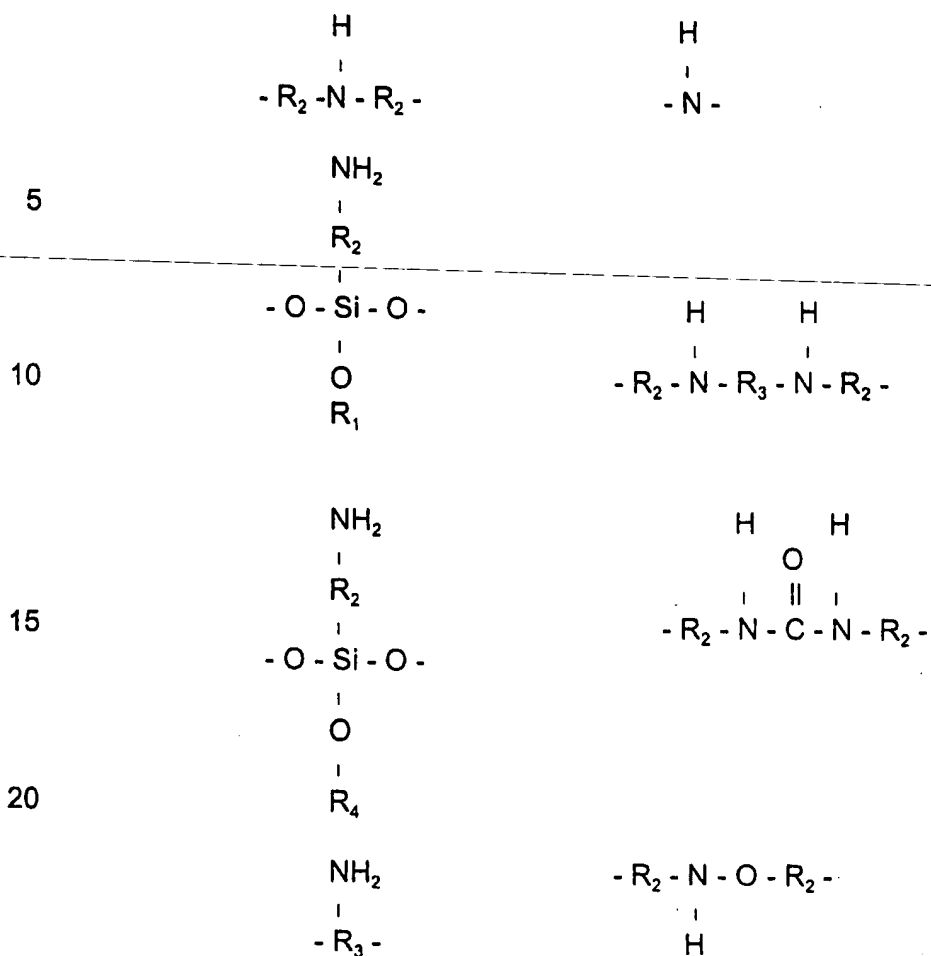
Wherein R_1 represents the same or different lower alkyls, generally C_1 to

C_5 and in particular C_1 to C_2 and wherein X is a nitrogen containing bridging group. The nitrogen will be a primary or secondary amine, a

ureido group, isocyanate or cyanide. Specific embodiments of X are as follows:

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12/17/98
tertiary amine

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Wherein R_2 is a lower alkenyl, R_3 represents alkenyl and substituted alkenyl wherein the substituents include acyl, amine, silyl, urethane, and R_4 represents an alkoxysilyl group.

Preferred compounds include:

bis [(3-trimethoxysilylpropyl)] amine
(A1170, OSI Specialties)

30 bis [(3-triethoxysilylpropyl)] amine
(B2492, United Chemicals)

1,4 bis [3-(trimethoxysilyl)propyl] ethylenediamine
(B2493, United Chemicals)

As indicated, the coating of the present invention can be applied to any galvanized surface. The galvanization process may leave an oily residue on the galvanized metal surface and it is preferable to remove this. This can be done using typical cleaners in particular caustic
5 cleaners such as Brent AC1055 cleaner available from Brent America Inc., Lake Bluff, IL (about 7.5% by weight, pH 12.5). Aqueous solutions of sodium hydroxide will also function.

The alkaline cleaner not only removes any oily residue but also improves the adhesion between the coating and the zinc and
10 ultimately the polymer and the zinc. Generally the galvanized surface is soaked or passed through the alkaline solution for a period of about 4 minutes or less with the bath temperature at 60° C.

The coating composition of the present invention can be applied in a variety of different concentrations from as little as .5% up to
15 100% i.e. without any water added). Generally it is preferable to disperse the coating composition into water or a water/alcohol blend. The preferred concentration level is generally from about 1% to about 5%.

Further the pH of the coating solution should be basic to maximize adhesion between the coating composition and the zinc. But
20 the pH should not exceed 9.5, or the coating composition will fall out of solution. Accordingly as the coating composition is mixed with water or water/alcohol, glacial acetic acid can be added to establish the pH of 6.5 to 9.5.

The adhesive promoting coating composition can be applied by spraying, dipping or brushing the coating composition onto the surface. With wire it is preferable to simply run the wire through a bath containing the coating composition. The coating composition is then dried and the surface is ready for application of the polymeric coating i.e., adhesive or paint.

The amount of the coating composition that is applied can vary widely. It generally will be about 100 angstroms in thickness although this is not believed to be critical for practicing the invention. In fact the coating composition does not have to be continuous in order to significantly improve the adhesion to the galvanized surface.

The polymeric coating can be in a form of either a thermoplastic or thermoset. Thermoplastic coatings particularly adhesives that will function in the present invention include ethylene acrylic acid copolymers, ethylene methacrylic acid copolymer and methyl acrylate and copolymers of acrylic acid derivatives such as methyl acrylate esters, ethyl acrylate and butyl acrylate esters, ethylene vinyl acetate copolymers, ethylene acrylic acid or ethylene methacrylic acid ionomers, maleic anhydride copolymers and derivatives, chlorinated polyethylene polyvinylchloride, polycarbonates, styrene/acrylic acid or methacrylic acid copolymers, acrylic and methacrylic resins, rubber modified polystyrenes as well as others.

Thermoset compositions that will adhere to the coated galvanized surface include epoxies, enamels, polyurethanes. Generally the more polar the polymer, the better the adhesion. However, even nonpolar polymers can be made to adhere to the coated galvanized surface by modification of the polymer with polar compatibilizing agents.

The present invention will be further appreciated in light of the following examples. To test the adhesion promoting compositions of the present invention, galvanized steel plates either electrogalvanized or hot-dipped as specified in the examples were coated as explained and subjected to either a 95% relative humidity test or a twenty minute rolling boil test. In the 95% relative humidity test the panels with the adhesive applied are subjected to 95% humidity for 72 hours. Generally two panels are tested each with three sections of adhesive per panel. After the 72 hours these are then allowed to come to ambient conditions and evaluated.

In the twenty minute rolling boil test, three cut specimens $\frac{1}{4}$ to $\frac{1}{2}$ inch wide with three sections of adhesive per specimen were immersed in water which was at a rolling boil. After twenty minutes they were removed, cooled for five minutes and evaluated.

The evaluation for both tests involved attempting to lift a section of the adhesive with a razor blade and then use this section to peel off the remaining adhesive. This was given a numerical value of from 0 to 4, 0 representing no adhesion, 1 representing weak adhesion,

2 representing moderate adhesion, 3 representing sufficient adhesion to cause the adhesive to break when pulled and 4 representing sufficient adhesion as to prevent the adhesive from being removed. The results were the averages of the number of sections of adhesives per specimen.

5 The panels tested were either cleaned or uncleaned panels.

The clean panels were prepared by immersing the panels for two minutes in 7.5% by weight solution of Brent AC1055 cleaner heated to a temperature of 60° C.

10 Different procedures were used to prepare the solutions of silane compositions. The compositions tested included bis [3-(trimethoxysilyl) propyl] amine which is referred to hereinafter by its trade designation of A-1170, 3-amino propyltris (trimethylsiloxy) silane referred to hereinafter as A-0805 and 1, 4 bis [3-(trimethoxysilyl) propyl] ethylenediamine referred to hereinafter as B-2492.

15 With respect to the A-1170 silane, this can be either used in a diluted concentration or as 100%. When the diluted silane was used, the percentage i.e., 3% would be added slowly to water adjusting the pH with glacial acetic acid to maintain a pH range of 6.7 to 9.5.

20 The panels would be coated by dipping the panels into the silane solution and holding them for thirty seconds. Excess coating at the bottom of the panel is removed with a towel or dry compressed air i.e., "de-teared", dried at 100° C. for ten minutes and the adhesive applied.

When 100% of the A-1170 silane was used, two to five drops were simply placed on the surface of the panel and spread to uniform thickness with a paper towel or other leveling device and heated to 120° to 150° C. for ten minutes to dry.

5 The B-2492 is sold as an alcohol solution (62% actives). This simply would be blended with about 3% water and the balance methanol with a pH maintained at a 6.7 to 9.5 with glacial acetic acid. The panels would be coated as described with respect to the diluted A-1170. When 100% of B-2492 is used, it would be applied to the panels
10 as described above with respect to the undiluted A-1170.

Panels were tested to determine the effect of metal surface pretreatment with a caustic solution i.e., Brent AC1055. The first series of panels listed on Table 1 were not treated with Brent AC1055 whereas the remaining four sets of panels were treated with Brent AC1055.

15 In all of these examples, the adhesive applied was ethylene acrylic acid copolymer. Specifically Primacor 3460 brand sold by Dow Chemical Company applied at 150° C and rolled on with pressure roller with minimal pressure.

TABLE 1

Effect of Metal Surface Pretreatment on Silane Adhesion Promoter Effectiveness
Adhesion of EAA Hot Melt Tape at 150° C to EZG60 Electrogalvanized Panels
All Panels Degreased with Isopropanol
pH of Aqueous Treatment = 7.5 - 8.5

5

		72-Hour 95% RH	20 Minute Water Boil
	Control	1	1
10	3% A-1170 No pretreatment	1	1
	5% A-1170 No pretreatment	1.5	1
	7.5% A-1170 No pretreatment	1	1
15	10% A-1170 No pretreatment	3	2
	100% A-1170 No pretreatment	4	1
20	100% B2493 No pretreatment	4	4
	Control Brent 1055	3	2
	3% A-1170 Brent 1055	4	4
25	3% B2493 Brent 1055	4	4
	100% A-1170 Brent 1055	4	4

These tests indicate that the caustic pretreatment significantly improves
 adhesion and thereby reduces the concentration of the silane required to

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improve adhesion. Without pretreatment excellent results were obtained only using at least 10% and preferably 100% of the A-1170 or 100% of the B2493. Whereas with the caustic pretreatment 3% of the A-1170 or B2493 produced excellent results.

5 Table 2 shows the effect of the pH of the A-1170 solution. The test panels were all cleaned with isopropanol and then treated with the caustic Brent AC1055. Both electrogalvanized steel panels and hot-dipped steel panels were tested. These tests demonstrate that the best results are achieved between pH 6.7 and 8.5.

10

TABLE 2

3% Aqueous Silane Treatment
Cleaned Isopropanol, Brent 1055, 7.5%, 60° C.
95% RH, 40° C.

		<u>Electrogalvanized</u>	<u>Hot-Dip</u>
15	No Treatment	2.5	3.5
	pH 4.0	2	2
	pH 5.5	3	3.5
	pH 6.7	4	3.5
	pH 8.5	4	4

20

The silane coating composition can also be applied to the metal surface in combination with a process lubricant. This would be most useful for coating drawn metal such as drawn wire. In these tests the process lubricant, which was primarily mineral oil with emulsifiers, was combined with a 3% aqueous solution of the A-1170 silane. Panels that

had been cleaned with the isopropanol and Brent 1055 at 7.5% for 60° C. were tested. As shown below, excellent results are obtained at a variety of concentrations of the process lubricant.

TABLE 3

5	3% Aqueous A-1170 Silane Formulated with Process Lubricant EZG60 Electrogalvanized Panels Cleaned Isopropanol, Brent 1055, 7.5%, 60° C.		
10		72-Hour 95% RH <u>40° C.</u>	20 Minute <u>Boil</u>
15	Untreated	3	2
	0% Process Lubricant	4	4
	5% Process Lubricant	3.8	3
	10% Process Lubricant	4	4
	20% Process Lubricant	4	4

20 Thus the present invention has a wide variety of applications and can be utilized to improve adhesion between a variety of adhesives and not only galvanized metals but also steel, brass and aluminum as well as either electroplated or hot dipped galvanized surfaces. It can be utilized on flat metal surfaces as well as drawn wire. This basically

25 eliminates the effect of humidity on adhesion to galvanized surfaces.

This has been a description of the present invention along with the preferred method of practicing the present invention. However,

the invention itself should be defined only by the appended claims
wherein we claim:

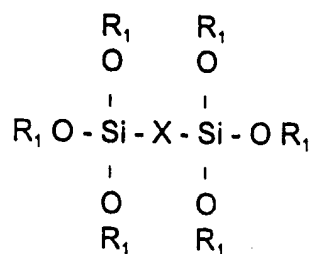
1. A method of improving adhesion to a metal surface applying an effective amount of an adhesion promoter onto said surface, said adhesion promoter comprising a compound having at least two alkoxy silyl groups bonded together by a bridging group said bridging group having at least one reactive nitrogen.
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2. The method claimed in claim 1 wherein said metal surface is a galvanized metal surface.

3. The method claimed in claim 2 wherein said adhesion promoting compound has the following general formula:

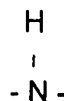
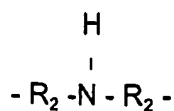
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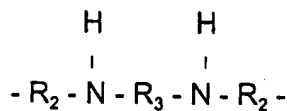
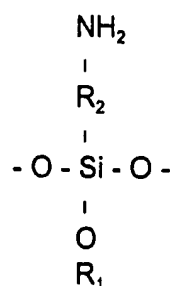
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4. The method claimed in claim 3 wherein X is selected from the group consisting of:

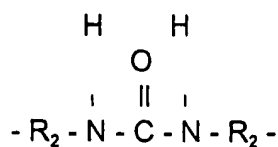
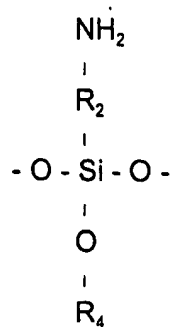
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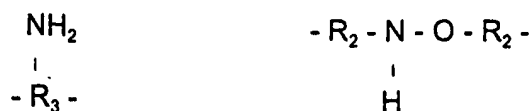


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wherein R_2 is a lower alkenyl, R_3 represents alkenyl and substituted alkenyl and R_4 represents alkoxysilyl.

- 5 5. The method claimed in claim 2 wherein said adhesion promoting compound is dissolved in the polar solvent selected from the group consisting of water and a mixture of water and alkyl alcohol.
- 10 6. The method claimed in claim 4 wherein said adhesion promoting compound is applied as a concentration of about 0.1 to about 100%.
7. 7. The method claimed in claim 2 wherein said galvanized metal surface is pretreated with an alkaline cleaner.
8. 8. The method claimed in claim 2 wherein said adhesion promoter is Bis [3-(trimethoxysilyl) propyl] amine.
- 15 9. The method claimed in claim 2 wherein said adhesion promoting compound is 3 - aminopropyl tris (trimethylsilyl) silane.
10. 10. The method claimed in claim 2 wherein said adhesion promoting compound is Bis [3 - (triethoxysilyl) propyl] amine.

11. The method claimed in claim 3 wherein said surface is further coated with a polymer.

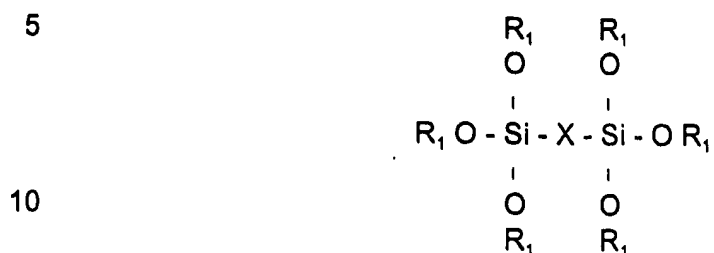
12. The method claimed in claim 11 wherein said polymer is a thermoplastic polymer.

5 13. The method claimed in claim 12 wherein said polymer is selected from the group consisting of ethylene acrylic acid copolymers, ethylene methacrylic acid copolymer, methyl acrylate, methyl acrylate esters, ethyl acrylate esters, butyl acrylate esters, ethylene vinyl acetate copolymers, ethylene acrylic acid ionomer, ethylene methacrylic acid ionomer, maleic
10 anhydride copolymers, chlorinated polyethylene and polyvinylchloride.

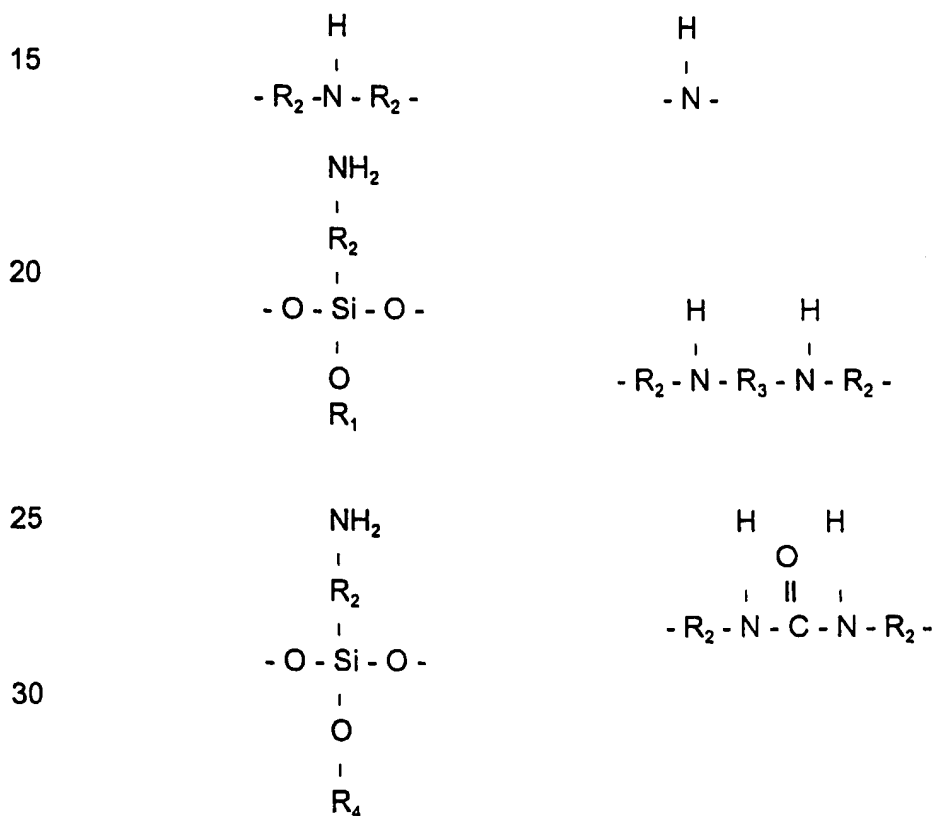
14. A metal surface having an adhesion promoting coating, said adhesion promoting coating comprising a compound having at least two alkoxy silane groups bonded together by a bridging group said bridging group including at least one reactive nitrogen.
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15. The metal surface claimed in claim 14 wherein said surface is galvanized.

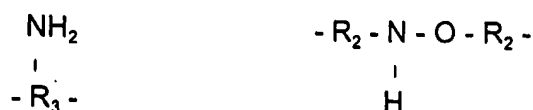
16. The galvanized surface claimed in claim 15 wherein said adhesion promoting compound has the following general formula:



17. The galvanized surface claimed in claim 16 wherein X is selected from the group consisting of:



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wherein R_2 represents a lower alkenyl, R_3 represents alkenyl

5 and substitute alkenyl and R_4 represents alkoxysilyl.

18. The galvanized surface claimed in claim 15 wherein said adhesion promoter is Bis [3-(trimethoxysilyl) propyl] amine.

19. The galvanized surface claimed in claim 15 wherein said adhesion promoting compound is 3 - aminopropyl tris (trimethylsiloxy) silane.

10 20. The galvanized surface claimed in claim 15 wherein said adhesion promoting compound is Bis [3 - (triethoxysilyl) propyl] amine.

21. The galvanized surface claimed in claim 15 wherein said surface is further coated with a polymer.

INTERNATIONAL SEARCH REPORT

In tional App. No.
PCT/US 99/36378

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B05D3/10 C23C22/68 C09J5/02

According to International Patent Classification (IPC) or to both national classification and IPC

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Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B05D C23C C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 687 882 A (BISHOP ERNEST M) 29 August 1972 (1972-08-29) the whole document	1
A	FR 1 207 887 A (UNION CARBIDE) 19 February 1960 (1960-02-19) the whole document	1
A	-& FR 77 326 E (UNION CARBIDE) 27 June 1962 (1962-06-27) the whole document	1

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☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No

P 99/30978

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3687882 A	29-08-1972	CA 980930 A	30-12-1975
		DE 2219691 A	09-11-1972
		FR 2134706 A	08-12-1972
		GB 1396403 A	04-06-1975
		IT 961292 B	10-12-1973
		JP 1313457 C	28-04-1986
		JP 55115472 A	05-09-1980
		JP 60031229 B	20-07-1985
		JP 55050078 B	16-12-1980
		NL 7205187 A,B,	31-10-1972
		NL 8602702 A,C	02-02-1987
		SE 379062 B	22-09-1975
FR 1207887 A	19-02-1960	FR 77326 E	27-06-1962
		GB 872929 A	
		GB 886453 A	
		US 3088847 A	07-05-1963